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13. ABSTRACT (Maximum 200 words)

The reaction of a toluene solution of $ZnEt_2$ with one equivalent of sulfur ($1/8 S_8$) results in dissolution of the sulfur to form a colorless solution. After addition of *n*-pentane and cooling, colorless crystals of $Zn_{10}(SEt)_{10}Et_{10}$ were isolated and characterized by a variety of spectroscopic characterization techniques and by single-crystal X-ray diffraction. Crystallographic data for $Zn_{10}(SEt)_{10}Et_{10}$ at 293K: space group $P\bar{1}$, $a = 12.010(2) \text{ \AA}$, $b = 14.739(3) \text{ \AA}$, $c = 20.327(4) \text{ \AA}$, $\alpha = 99.93(3)^\circ$, $\beta = 91.62(3)^\circ$, $\gamma = 107.79(3)^\circ$, $V = 3362.2(11) \text{ \AA}^3$, $Z = 2$, $d(\text{calc}) = 1.636 \text{ g/cm}^3$, $R = 9.41\%$, $R_w = 9.00\%$. Although the crystal deteriorated during data collection, the structural data show that $Zn_{10}(SEt)_{10}Et_{10}$ exhibits a unique wurtzite-like ZnS core rather than a sphalerite-like core which is more common to zinc and cadmium alkylthiolate clusters. Thermal decomposition of $Zn_{10}(SE)_{10}Et_{10}$ was studied by diffraction methods, microscopy, thermal analysis and elemental analysis. These data are consistent with the formation of a crystalline, cubic (sphalerite) ZnS at low temperatures, 250°C , providing evidence that the structure of the molecular precursor *does not* direct the crystallization of a particular polymorph on solid-state thermolysis in this system.

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Synthesis and Characterization of $[\text{Zn}(\text{SEt})\text{Et}]_{10}$, Formed via Insertion of
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by

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Synthesis and Characterization of $[\text{Zn}(\text{SEt})\text{Et}]_{10}$, Formed via Insertion of Sulfur into Zn-C Bonds: A New Class of Wurtzite-like Cluster Framework.

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Abstract:

The reaction of a toluene solution of ZnEt_2 with one equivalent of sulfur ($1/8 \text{ S}_8$) results in dissolution of the sulfur to form a colorless solution. After addition of *n*-pentane and cooling, colorless crystals of $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ were isolated and characterized by a variety of spectroscopic characterization techniques and by single-crystal X-ray diffraction. Crystallographic data for $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ at 293K: space group $\text{P}\bar{1}$, $a = 12.010 (2) \text{ \AA}$, $b = 14.739 (3) \text{ \AA}$, $c = 20.327 (4) \text{ \AA}$, $\alpha = 99.93 (3)^\circ$, $\beta = 91.62 (3)^\circ$, $\gamma = 107.79 (3)^\circ$, $V = 3362.2 (11) \text{ \AA}^3$, $Z = 2$, $d(\text{calc}) = 1.636 \text{ g/cm}^3$, $R = 9.41\%$, $R_w = 9.00\%$. Although the crystal deteriorated during data collection, the structural data show that $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ exhibits a unique wurtzite-like ZnS core rather than a sphalerite-like core which is more common to zinc and cadmium alkylthiolate clusters. Thermal decomposition of $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ was studied by diffraction methods, microscopy, thermal analysis and elemental analysis. These data are consistent with the formation of a crystalline, cubic (sphalerite) ZnS at low temperatures, 250°C , providing evidence that the structure of the molecular precursor *does not* direct the crystallization of a particular polymorph on solid-state thermolysis in this system.

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Metal thiolate compounds exhibit a rich and interesting structural chemistry that has been studied extensively.¹⁻⁶ These complexes are of scientific and technological interest as a result of their structural similarity to metalloproteins, metallothioneins⁷ and the possibility that they can be used as precursors for the formation of binary metal sulfides.⁸⁻¹¹ Furthermore, as a result of the tendency of these species to oligomerize,^{3-6,12,13} recent interest has focused on the formation of large molecular aggregates, often containing sulfide ligands, S²⁻,¹⁴⁻²³ which exhibit interesting optical and electronic properties.²⁴ Large Zn and Cd alkyl thiolate and sulfide clusters are of particular interest because they generally exhibit a core structure that is analogous to that of the bulk, sphalerite-phase metal sulfide, as shown in Figure 1.³ As a result, they can be used to test structural theories because these species should exhibit properties that are intermediate between those of nanometer-sized metal sulfide particles²⁵ and those of discrete molecular species.²⁴ In this paper we describe the synthesis, characterization and thermal decomposition of a new molecular zinc thiolate cluster, Zn₁₀(SEt)₁₀Et₁₀, formed via the insertion of sulfur into half the metal-carbon bonds of ZnEt₂. In contrast to other examples of Zn and Cd alkyl thiolate clusters, this species exhibits a new molecular structural architecture, more closely related to wurtzite than to sphalerite-phase ZnS.

The reaction of a toluene solution of ZnEt₂ with one equivalent of sulfur (1/8 S₈) results in dissolution of the sulfur to form a colorless solution (see Supplementary Materials for synthesis and characterization data). After addition of *n*-pentane and cooling, colorless crystals were isolated that have empirical formula, [Zn(SEt)Et] as determined by elemental analysis. The ¹H and ¹³C NMR spectroscopy were also consistent with this empirical formula, showing the presence of a large number of different types of overlapping Zn-Et and Zn-SEt resonances which could not be distinguished even at high fields. The insertion of sulfur into metal carbon bonds has recently been reported for the case of Grignard-type reagents, but has not been extensively studied for other metal carbon bonds.¹ The reaction of S₈ with transition metal complexes generally leads to the formation

of metallapolysulfane complexes containing polysulfide (S_x)²⁻ chains.^{8,26-28} Characterization of the crystals isolated from this reaction by single-crystal X-ray diffraction revealed the molecular formula, $Zn_{10}(SEt)_{10}Et_{10}$. The structure of this molecule is shown in Figure 2a and consists of three six-membered, chair conformation Zn-S rings each linked together through three Zn-S bonds with capping SEt and Zn-Et groups at each end respectively.* This structural unit bears a striking resemblance to the wurtzite structure of bulk crystalline ZnS, as shown by comparison to the $[ZnS]_9$ wurtzite fragment drawn in Figure 2b.^{29,30} To our knowledge, this is the first example of the observation of a wurtzite-like core structure in a zinc or cadmium thiolate cluster. Unfortunately, the quality of the structural data does not warrant a detailed discussion of the metrical parameters of this molecule, but the Zn-S and Zn-C bond lengths are in the normal range (see Supplementary Materials). Numerous attempts to obtain better crystals and better quality crystallographic data at low temperatures did not result in better quality data than that reported here.

Other examples of compounds with empirical formula $[Zn(SR)R']_n$ have been prepared by the reaction of ZnR'_2 with one equivalent of HSR.³¹ The species that have been structurally characterized, $[MeZn(S-*t*-Bu)]_5$ ³² and $[MeZn(S-*i*-Pr)]_8$ ³³ do not resemble either sphalerite or wurtzite structures. However, it is interesting to note that the species found in the solid state to be $[MeZn(S-*i*-Pr)]_8$ ³³ is hexameric in benzene solution. At this stage, it is not clear whether the molecular integrity of $Zn_{10}(SEt)_{10}Et_{10}$ is retained in solution, although the complexity of the ¹H and ¹³C NMR data is consistent with the presence of this molecule.

As a result of the unusual wurtzite-like core structure of $Zn_{10}(SEt)_{10}Et_{10}$ and the

* Crystallographic data for $Zn_{10}(SEt)_{10}Et_{10}$ at 293K: space group $P\bar{1}$, $a = 12.010(2)\text{\AA}$, $b = 14.739(3)\text{\AA}$, $c = 20.327(4)\text{\AA}$, $\alpha = 99.93(3)^\circ$, $\beta = 91.62(3)^\circ$, $\gamma = 107.79(3)^\circ$, $V = 3362.2(11)\text{\AA}^3$, $Z = 2$, $d(\text{calc}) = 1.636\text{ g/cm}^3$, $R = 9.41\%$, $R_w = 9.00\%$. Data was collected from three different samples of crystals obtained from three independent reactions and grown from various solvents. Although the refinement value is poor due to deterioration of the sample during data collection, this is the best data set available. See supplementary data for details.

fact that wurtzite-type ZnS is the high temperature ($> 1000^{\circ}\text{C}$) thermodynamically stable crystalline phase of ZnS,²⁹ we examined the thermal decomposition behavior of this molecular aggregate. However, it was anticipated that if the normal metal thiolate thermal decomposition pathway was followed, which involves elimination of alkyl sulfides (see equation 1), then a sulfur-deficient product should be formed.



The compound $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ was heated under inert atmosphere to 250, 350, 450 and 700 $^{\circ}\text{C}$ for 30 min. in separate experiments. Thermogravimetric analysis data revealed a slightly larger weight loss (39%) than expected (37%) for the formation of ZnS. X-ray diffraction data showed the presence of crystalline material with broad peaks corresponding to ~ 2 nm sized crystallites on heating to only 250 $^{\circ}\text{C}$.³⁴ At higher temperatures, the peaks were sharper and corresponded to cubic (sphalerite) ZnS (see Figure 3) analogous to the results observed previously for the reaction between H_2S and $[\text{EtZnS-t-Bu}]_5$.³⁵ TEM data gave analogous results. Analysis of the volatile byproducts formed on thermal decomposition at 350 $^{\circ}\text{C}$ showed the presence of C_2H_4 , C_2H_6 , $\text{CH}_3\text{C}(\text{H})\text{S}$, and Et_2S providing evidence for elimination of some sulfur-containing products. These results provide evidence that the structure of the molecular precursor *does not* direct the crystallization of a particular polymorph on solid-state thermolysis in this system. This observation is in contrast to the GaS ³⁶ and InS ³⁷ systems where the structure of the metastable phases formed by chemical vapor deposition (CVD) were related to the structural framework of the precursor, although the role of substrate in directing the crystallization process is not clear.

Further studies are in progress to determine the generality of this sulfur-insertion reaction into other metal-carbon bonds and to understand the origin of the formation of the wurtzite core structure. We are also investigating the reactivity of $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ to

determine whether it is possible to use this species as a molecular building block to systematically prepare larger clusters with controlled size.

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Supplementary Materials Available: Synthesis and characterization data for $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$, (1 page). X-ray crystallographic data for $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$, Structure Determination Summary, Atomic Coordinates, Bond Lengths and Angles, Anisotropic Displacement Coefficients, H-Atom Coordinates, Isotropic Displacement Coefficients and Refinement Summary (19 pages). Observed and Calculated Structure Factors (16 pages).

References

- (1) Bonasia, P. J.; Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 6777.
- (2) *J. Electronic Materials: Special Issue on Wide-Bandgap II-IV Semiconductor Materials*; TMS: New York, 1993; Vol. 22, pp 429-577.
- (3) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.
- (4) Dance, I. G.; Garbutt, R. G.; Craig, D. C.; Scudder, M. L.; Bailey, T. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1164.
- (5) Dance, I. G.; Garbutt, R. G.; Bailey, T. D. *Inorg. Chem.* **1990**, *29*, 603.
- (6) Dance, I. G.; Garbutt, R. G.; Scudder, M. L. *Inorg. Chem.* **1990**, *29*, 1571.
- (7) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 769.
- (8) Muller, A.; Diemann, E. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987; Vol. 2, Chapter 16.1.
- (9) O'Brien, P. In *Inorganic Materials*; D. W. Bruce and D. O'Hare, Ed.; John Wiley & Sons Ltd.: 1992; pp 491.
- (10) Osakada, K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1117.
- (11) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240.
- (12) Craig, D.; Dance, I. G.; Garbutt, R. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 165.
- (13) Dance, I. G.; Scudder, M. L.; Secomb, R. *Inorg. Chem.* **1983**, *22*, 1794.
- (14) Lee, G. S. H.; Fisher, K. J.; Vassallo, A. M.; Hanna, J. V.; Dance, I. G. *Inorg. Chem.* **1993**, *32*, 66.
- (15) Lee, G. S. H.; Fisher, K. J.; Craig, D. C.; Scudder, M. L.; Dance, I. G. *J. Am. Chem. Soc.* **1990**, *112*, 6435.
- (16) Lee, G. S. H.; Craig, D. C.; Ma, I.; Scudder, M. L.; Bailey, T. D.; Dance, I. G. *J. Am. Chem. Soc.* **1988**, *110*, 4863.
- (17) Herron, N.; Wang, Y.; Eckert, H. *J. Am. Chem. Soc.* **1990**, *112*, 1322.
- (18) Herron, N.; Suna, A.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 2329.
- (19) Herron, N.; Calabrese, J. G.; Farneth, W. E.; Wang, Y. *Science* **1993**, *259*, 1426.

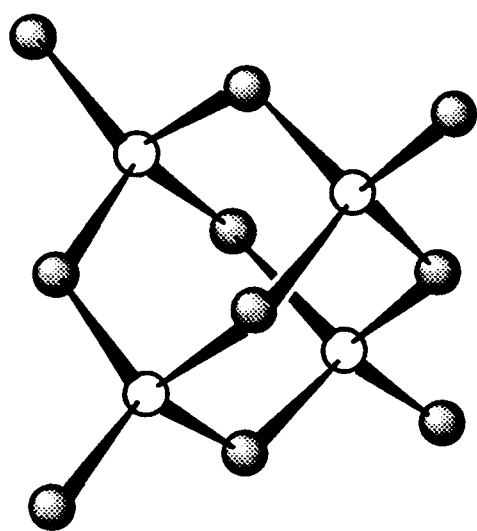
- (20) Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6825.
- (21) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183.
- (22) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403.
- (23) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141.
- (24) Yang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525.
- (25) Chandler, R. R.; Bigham, S. R.; Coffey, J. L. *J. Chem. Ed.* **1993**, in press.
- (26) Muller, A.; Diemann, E. *Adv. Inorg. Chem. Radiochem.* **1987**, *31*, 89.
- (27) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 742.
- (28) Banda, R. M. H.; Dance, I. G.; Bailey, T. D.; Craig, D. C.; Scudder, M. L. *Inorg. Chem.* **1989**, *28*, 1862.
- (29) Sharma, R. C.; Chang, Y. A. *Binary Alloy Phase Diagrams*; 2 ed.; Scott, W.W.: 1990; Vol. 3, pp 3297.
- (30) Evans, H. T.; McKnight, E. T. *The American Mineralogist* **1959**, *44*, 1210.
- (31) Bell, N. A.; Moseley, P. T. *J. Organomet. Chem.* **1987**, *325*, 47.
- (32) Adamson, G. W.; Bell, N. A.; Shearer, H. M. M. *Acta Cryst.* **1982**, *B 38*, 462.
- (33) Adamson, G. W.; Shearer, H. M. M. *Chemical Communications* **1969**, *16*, 897.
- (34) Cullity, B. D. *Elements of X-ray Diffraction*; 2nd ed.; Addison-Wesley: 1987.
- (35) Gupton, T. A.; Czekaj, C. L.; Rau, M. S.; Geoffroy, G. L.; Pantano, C. G. *Mat. Res. Soc. Symp. Proc.* **1988**, *121*, 503.
- (36) MacInnes, A. N.; Power, M. B.; Barron, A. R. *Chem. Mater.* **1993**, *5*, 1344.
- (37) MacInnes, A. N.; Cleaver, W. M.; Barron, A. R.; Power, M. B.; Hepp, A. F. *Adv. Mater. Opt. Electron.* **1992**, *1*, 229.

Figure Captions:

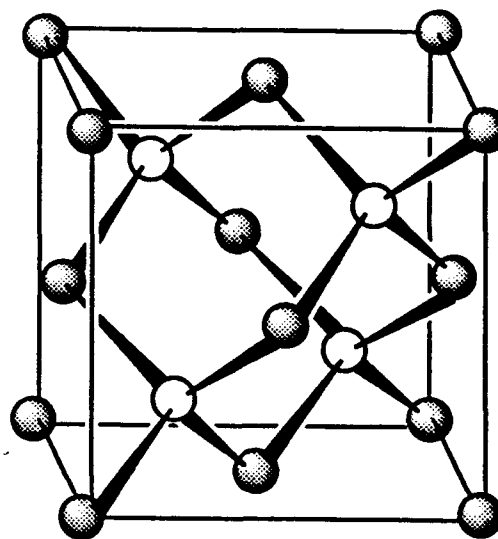
Figure 1: Comparison of (a) the adamantanoid fragment commonly found in metal alkyl thiolate compounds and (b) the cubic unit cell of sphalerite (taken from reference 3).

Figure 2: (a) Ball and stick drawing of the molecular structure of $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ emphasizing the geometry of the $[\text{ZnS}]_9$ core. (b) A portion of the structure of wurtzite ZnS .³⁰

Figure 3: X-ray powder diffraction data for the solid obtained by thermal decomposition of $\text{Zn}_{10}(\text{SEt})_{10}\text{Et}_{10}$ at 250-700 °C.



(a)



(b)

